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The dynamic polarizability of helium : inclusion of the rearrangement effect in an extended version of coupled Hartree Fock theory

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We propose here a possible method of extending the coupled-Hartree-Fock theory using ideas similar to the multipattern multi-configuratioon self-consistent field (MC-SCF) concept of Gilbert. The approach has been tested in its simplest form in calculating the dynamic polarizability of the helium atom. In the long wavelength region the theory predicts excellent values of the dynamic polarizability. The predicted value of the $1s^2$: ^1S -> 1s2p : ^1P transitional oscillator strength in this theory is in good agreement with the extended calculations of Weiss. Possible ways of simplifying and extending this approach to larger systems has been discussed.

1. INTRODUCTION

During the past few years, the coupled Hartree--Fock (CHF) approximation[1] has been extensively used for calculating the polarizabilities and other related properties of small and medium-sized atoms and ions. This method, which is physically equivalent to the Random Phase Approximation (RPA) cast in a non-orthogonal basis, yields fairly good values of polarizabilities with a none-too-extensive computational effort. For obtaining more accurate theoretical estimates of polarizabilities, various other approaches have been explored, prominent among which is the application of the linked Cluster many-body perturbation theory (LCMBT) by Kelly[2] and Das[3] and co-workers. Recently there have been some applications of the multi-configuration self consistent field (MCSCF) method[4], originally developed for handling the molecular correlation energy problem, in which a compact expansion of the total wave-function is sought in terms of a common set of optimized orbitals. This

approaches has been utilized by Billingsley and Krauss[5] for the polarizabilities of some atoms with extremely satisfactory results. Later Sanders[6] extended this approach to the case of dynamic polarizabilities, although he did not test the performance of his theory numerically. Very recently Gilbert[7] has propounded the so-called multi-pattern MCSCF idea, in which a further degree of flexibility is imparted to the MCSCF concept by waiving the requirement of a common set of orbitals for building the configurations. Instead, in his formalism, each configuration is characterized by its own set of orbitals. Gilbert's idea, again, has not been put to any numerical test so far.

In a recent publication[8] we proposed a simple extension of the CHF theory which closely parallels Gilbert's idea. A numerical application was made to calculate the static polarizability α_d of the He sequence of ions, with excellent results. In the present paper a similar extension of the CHF theory is proposed for computing the dynamic polarizabilities. The theory is developed here for the special case of two-electron ions, because our present intention is just to test the multi-pattern idea in the simplest possible form. Later we intend to cast the theory in a general form with the necessary modifications. As the basis for implementing the present scheme, we have utilized the time-dependent variation principle of Langhoff *et al.*[9] In this variation principle one first extracts the so-called secular and normalization terms from the total-time-dependent wavefunction, before attempting a perturbation expansion of the remaining regular part. In the following section we recall the salient features of this variation principle before going over to a discussion of the proposed extension of the CHF the ory.

2. The Time-Dependent Variation Principle

The Schrodinger equation in the presence of time-dependent perturbation is written as

$$\left((H_0(\mathbf{r}) + H_1(\mathbf{r},t) - \frac{i\delta}{\delta t}\right) \Psi(\mathbf{r},t) = 0 \qquad (1)$$

where $H_0(\mathbf{r})$ and $H_1(\mathbf{r},t)$ are respectively the unperturbed Hamiltonian and the perturbation term, $\Psi(\mathbf{r},t)$ time-dependent wavefunction.

Frenkel's time-dependent variation principle may be expressed as

$$\langle \delta\tilde{\Psi} \mid H_0 + H_1 - \frac{i\delta}{\delta t} \mid \tilde{\Psi} \rangle = 0 \qquad (2)$$

where $\tilde{\Psi}$ is a trial solution of eqn. (2) and $\delta\tilde{\Psi}$ is an arbitrary first order

variation about this solution. Adding to Eqn. (2) its complex conjugate we get

$$\delta\langle\tilde{\Psi} \mid H_0 + H_1 - \frac{i\delta}{\delta t} \mid \tilde{\Psi}\rangle + \frac{i\delta}{\delta t}\langle\tilde{\Psi} \mid \delta\tilde{\Psi}\rangle = 0 \qquad (3)$$

Following Langhoff *et al.*, we choose

$$\tilde{\Psi}(\mathbf{r},t) = \tilde{\Phi}(\mathbf{r},t) \exp\left[-i\int_{-\infty}^{t} K(\tilde{\Phi})\, dt'\right], \qquad (4)$$

where

$$K(\tilde{\Phi}) = \langle\tilde{\Phi} \mid H_0 + H_1 - \frac{i\delta}{\delta t} \mid \tilde{\Phi}\rangle / \langle\tilde{\Phi} \mid \tilde{\Phi}\rangle$$

$\tilde{\Phi}$ being the regular part of the trial function. For a perturbation periodic in time we demand that $\tilde{\Phi}$ satisfy the periodicity condition

$$\tilde{\Phi}(t+\tau) = \tilde{\Phi}(t),$$

τ being the period of the applied perturbation. Inserting eq. (4) in eq. (3), and using this periodicity condition, we get after time averaging

$$\delta\{\mathrm{Re}\ K(\tilde{\Phi})\} = 0 \qquad (5)$$

where $\{\mathrm{Re}\ K(\tilde{\Phi})\} \equiv \frac{1}{\tau}\int_{t}^{t+\tau} \mathrm{Re}\, K(\tilde{\Phi})\, dt$

We shall use eq. (5) to find the linear response of the system under the influence of an external perturbation. We may point out here that this variation principle (eq. (5)) provides upper bounds to the dynamic polarizability in the first transition region, which was not true of the Frenkel variation principle, eq. (2). In the following sections we shall be concerned only with the regular part of the total wavefunction.

3. The Dynamic Polarizability of Helium

The non-relativistic Hamiltonian for the He atom (in atomic units) is given by

$$H_0 = \sum_{i=1,2} \left(-\frac{1}{2}\nabla_i^2 - \frac{2}{r_i} \right) + \frac{1}{r_{12}}$$

$$= \sum_{i=1,2} \delta_i + g_{12} \text{ in the fixed nucleus approximation.}$$

Let us consider the atom to be placed in an external oscillatory electrical field, assumed to be directed along the z- axis for convenience,

$$E=(0, 0, E_z) ; \; E_z = 2E_0 \cos \omega t,$$

ω being the frequency. The interaction Hamiltonian is then given by

$$H_1 = 2 \sum_{i=1,2} h_i \cos \omega t ; \quad h_i = E_0 z_i. \tag{7}$$

Z_i being the Z-coordinate of the ith electron.

In the restricted Hartree-Fock (HF) approximation, the regular part of the singlet ground state wavefunction is given by

$$\Phi_0 (1,2) = \pi_{i=1,2} \phi_0 (i) \wedge (1,2) \tag{8}$$

where Φ_0 is the normalized single-particle HF occupied orbital, and Λ (1,2) is the normalized spin function

$$\wedge (1,2) = \frac{1}{\sqrt{2}} (\alpha (1) \beta (2) - \beta (1) \alpha (2)). \tag{9}$$

In the presence of the external perturbation H_1, we first assume a trial function of the same form as (12)

$$\Phi (1,2) = \pi_{i=1,2} \phi (i) \wedge (1,2) \tag{10}$$

As in the case of the CHF approximation, we now assume that each of the orbitals is perturbed upto first order in the external field, so that

$$\phi \simeq \phi_0 + \delta \phi_0 \tag{11}$$

where $\delta\phi_0$ is proportional to E_0, and has angular symmitry $Z(\bar{\chi})\,\Phi_0$. In the present case the occupied orbital has a γ_0^0 symmetry, so that $\delta\Phi_0$ is simply proportional to γ_1^0. We thus express $\delta\phi^0$ as

$$\delta\phi_0 = E_0 \left(\delta\phi^+{}_0 + e^{-i\omega t} + \delta\phi^-{}_0 e^{-i\omega t} \right), \text{ where } \delta\phi_0{}^+ \text{ and } \delta\phi_0{}^- \tag{12}$$

are trial functions to be determined, Introducing the operator P_{12} which interchanges the coordinates 1 and 2 and $Q_{12} = 1 + P_{12}$, we may express Φ (1,2) as

$$\Phi(1,2) = \underset{1,2}{\pi}\,\phi_0(i) + Q_{12}\left(\delta\phi_0(1)\,\phi_0(2)\right) + \underset{i=1,2}{\pi}\,\delta\phi_0(i) \tag{13}$$

We shall henceforth drop the spin function Λ (1,2), because there are no spin dependent operators in H_0 and H_1. In this form the wavefunction Φ (1,2) corresponds to the CHF approximation.

Let us now separately examine the different terms in eq. (13). The configuration $\underset{1-1,2}{\pi}\phi_0(i)$ is a self-consistent one since ϕ_0 is the occupied HF orbital. From the point of view of self consistency there is an error in the configuration $Q_{12}\ (\delta\phi_0(1)\phi_0(2)$ for the following reason. This configuration corresponds to a situation in which an electron has been excited out of the core configuration $\underset{i=1,2}{\pi}\phi_0(i)$. Physically speaking, as a result of this excitation, the nucleus experiences lowered screening, due to which the remaining core electron feels enhanced attraction by the nucleus. The occupied orbital in the singly excited configuration will tend to contract spatially as a result. We shall call this the *rearrangement effict* To include this effect, we accordingly de-freeze the occupied orbital ϕ_0 in the configuration $Q_{12}(\delta\phi^0(1)\ \phi^0(2))$, so that the new trial wavefunction becomes

$$\tilde{\Phi}(1,2) = \underset{i=1,2}{\pi}\,\phi_0(i) + Q_{12}\left(\delta\phi_0(1)\,\phi_0{}'(2)\right) + \underset{i=1,2}{\pi}\,\delta\phi_{10}(i) \tag{14}$$

where $\phi_0{}'$ is a new normalized occupied orbital. In this form the configuration interaction wavefunction Φ (1,2) resembles Giibert's multi-pattern function: moreover, as we cannot now combine the three configurations on the right

hand side of eq. (14) into a single configuration, in eq. (13), the function Φ (1,2) is expected to bring in additional dynamical correlation effects over and above those present in the CHF theory.

With the trial form (14), and using eq. (12) for $\delta\Phi_0$, the expression for Re $k(\tilde{\Phi})\}$ becomes

$$\begin{aligned}\{\mathrm{ReK}(\tilde{\Phi})\} = {} & E_{HF} + E_0^2 \{2\,[\langle\delta\phi_0^+|f|\delta\phi_0^+\rangle + \langle\delta\phi_0^-|f|\delta\phi_0^-\rangle] \\ & - 2\,(\varepsilon_0+\omega)\,\langle\delta\phi_0^+|\delta\phi_0^+\rangle - 2\,(\varepsilon_0-\omega)\,\langle\delta\phi_0^-|\delta\phi_0^-\rangle \\ & + 4\,\langle\phi_0|\phi_0'\rangle\,[\langle\phi_0|h|\delta\phi_0^+\rangle + \langle\phi_0|h|\delta\phi_0^-\rangle] \\ & + 2[\langle\phi_0'|f|\phi_0'\rangle - \langle\phi_0|f|\phi_0\rangle]\,(\langle\delta\phi_0^+|\delta\phi_0^+\rangle + \langle\delta\phi_0^-|\delta\phi_0^-\rangle) \\ & + 2\,\{\langle\phi_0'\delta\phi_0^+|g_{12}\,Q_{12}|\,\phi_0'\delta\phi_0^+\rangle + \langle\phi_0'\delta\phi_0^+|g_{12}\,Q_{12}|\,\phi_0'\delta\phi_0^-\rangle\} \\ & + 4\,\langle\phi_0\phi_0|g_{12}|\,\delta\phi_0^+\delta\phi_0^-\rangle\ . \end{aligned} \tag{15}$$

where we have retained upto terms proportional to E_0^2. ε_0 in eq. (15) is the HF energy corresponding to the orbital Φ_0, as given by Koopmans' theorm, and E_{HF} the total HF energy. To recover the CHF approximation, we set $\phi_0' = \phi_0$ in Eqn. Φ

We shall henceforth drop E_{HF} from eq (15) as it is a constant and does not participate in the variation. Expression (15) contains two kinds of variation elements, the functions $\delta\phi^+_0$, $\delta\phi^-_0$ and ϕ_0'. The problem of optimizing $\{\mathrm{ReK}(\tilde{\Phi})\}$ against variations in these functions is briefly discussed in the following section.

4. Optimization of $\{\mathrm{ReK}(\tilde{\Phi})\}$

To optimize the functional $\{\mathrm{ReK}\,\tilde{\Phi}\}$ we have to carry out unrestricted variation with respect to the functions $\delta\phi_0^+$ and $\delta\phi_0^-$, and also with respect to the core function ϕ_0', subject to the condition that ϕ_0' stays normalized during the variation. The overall variation problem is a non-linear one, and is carried out in two steps.

We first analytically represent the functions $\delta\phi_0^+$ and $\delta\phi_0^-$ in some appropriate basis

$$\delta\phi_0 = \Sigma\, c_i\ \psi_i\ Y_i^{\nu}\ . \tag{16}$$

Ψ_i's are the basis functions, and chosen in this case to be Slater type orbitals (STO).

$$\psi_i = N_i\, r^{n_i - 1} e \times p\,(-\zeta_i r); \qquad N_i = \frac{(2\zeta_i)^{n_i + \frac{1}{2}}}{\sqrt{(2n_i)!}} \tag{17}$$

To get adequate convergence with a fairly compact set, it is necessary to optimize the screening parameters ζ_i, which is rather costly in terms of computer time. In this preliminary calculation we have used instead a fairly large basis set consisting of eight STO functions for each of $\delta\phi_0^+$ and $\delta\phi_0^-$, with unoptimized screening parameters.

The problem of normalization constrained variation of may be tackled in two ways. One is choose the variation of ϕ_0' in the form

$$\delta\phi_0' = \Delta\phi_0' - \langle \Delta\phi_0' \mid \phi_0' \rangle \phi_0' \tag{18}$$

so that $\langle \delta\phi_0' \mid \phi_0' \rangle = 0$, $\Delta\phi_0'$ being any arbitrary variation. This leads to somewhat complicated non-linear equations, and hence we opt for a very simple, though approximate, method. We adopt the perturbation spirit, and express ϕ_0' as

$$\phi_0' = N' (\phi_0 + \delta\phi_0') \tag{19}$$

where ϕ_0 is the occupied HF orbital, and N′ the normalization factor. We now impose the constraint

$$\langle \phi_0 \mid \delta\phi_0' \rangle = 0, \text{ so that } N' = (1 + \langle \delta\phi_0' \mid \delta\phi_0' \rangle)^{-\frac{1}{2}}. \tag{20}$$

Expanding N′ binomially, and retaining terms upto quadratic in $\delta\phi_0'$ we have

$$\phi_0' = \phi_0 + \delta\phi_0' - \tfrac{1}{2} \langle \delta\phi_0' \mid \delta\phi_0' \rangle \phi_0. \tag{21}$$

This is a valid approximation if $\langle \delta\phi_0' \mid \delta\phi_0' \rangle$ is small, and this expectation is borne out in the actual calculations. For the occupied orbital ϕ_0, we have used the compact 4-parameter basis of Clementi[10]. Since the functions ϕ_0 and ϕ_0' differ only slightly, the basis set which is optimal for ϕ_0 should also be near optimal for $\delta\phi_0'$. We have thus expressed

$$\delta\phi_0' = \Sigma D_i \chi_i \tag{22}$$

where χ_i's are Clementi's basis functions.

For every frequency the optimization is carried out through the following steps of iteration :

(1) We first put $\phi' = \phi_0$ in eq. (15), so that $\{\mathrm{ReK}(\Phi)\}$ reduces to $\{\mathrm{ReK}_{\mathrm{CHF}}(\Phi)\}$. Using retresentation (16) for $\delta\Phi_0^+$ we get a form containing terms both linear and quadratic in the unknown coefficients $C_i^{\pm}$. A linear variation of this form with respect to those coefficients yields simultaneous equations of the type

$$\mathbf{A}(\omega)\,\mathbf{C} = \lambda$$

where $\mathbf{C}$ is a column matrix of the coefficients $C_i^{\pm}$ and λ is a constant column matrix. We then have

$$\mathbf{C} = \mathbf{A}^{-1}\omega\,\lambda \tag{23}$$

The coefficients $C_i^{\pm}$ emerging at this stage correspond to the CHF approximation.

(2) We now substitute relation (21) in the expression for ϕ_0' to obtain

$$\{\mathrm{ReK}(\tilde{\Phi})\} = \{\mathrm{ReK}_{\mathrm{CHF}}(\Phi)\} + \mathrm{L} \tag{24a}$$

where $\mathrm{L} = -2\,\langle\phi_0|h|\delta\phi_0^+ + \langle\phi_0|h|\delta\phi_0^-\rangle\langle\delta\phi_0'|\delta\phi_0'\rangle$

$-2(\langle\delta\phi_0^+|\delta\phi_0^+ + \langle\delta\phi_0^-|\delta\phi_0^-\rangle)(\langle\delta\phi_0'|f|\phi_0 + \langle\phi_0|f|\delta\phi_0'\rangle)$

$-2\langle\phi_0|f|\phi_0\rangle(\langle\delta\phi_0^+|\delta\phi_0^+\rangle + \langle\delta\phi_0^-|\delta\phi_0^-\rangle)\langle\delta\phi_0'|\delta\phi_0'$

$+2(\langle\delta\phi_0^+|\delta\phi_0^+\rangle + \langle\delta\phi_0^-|\delta\phi_0^-\rangle)\langle\delta\phi_0'|f|\delta\phi_0'\rangle$

$+2[\langle\delta\phi_0'\delta\phi_0^+|g_{12}\,Q_{12}|\phi_0\delta\phi_0^+\rangle + \langle\phi_0\delta\phi_0^+|g_{12}\,Q_{12}|\delta\phi_0'\delta\phi_0^+\rangle$

$+\langle\delta\phi_0'\delta\phi_0^-|g_{12}\,Q_{12}|\phi_0\,\delta\phi_0^-\rangle + \langle\phi_0\,\delta\phi_0^-|g_{12}Q_{12}|\delta\phi_0'\delta\phi_0^-\rangle]$

$-2\langle\delta\phi_0'|\delta\phi_0'\rangle[\langle\phi_0\delta\phi_0^+|g_{12}Q_{12}|\phi_0\delta\phi_0^+\rangle + \langle\phi_0\delta\phi_0^-|g_{12}Q_{12}|\phi_0\phi_0^-\rangle]$, 24b)

where again we ignore terms higher than quadratic in $\delta\phi_0'$. This again rests on the assumption that $\delta\phi_0'$ is small. We now subsitute the representations of $\delta\phi_0^+$ and $\delta\phi_0^-$ found from step (1) above, treating them as known quantities. Using eq. (22) to represent $\delta\phi_0'$, we obtain a form which upon variation of the coefficients D_i yields equations of the form

$$\mathbf{B}(\omega)\,\mathbf{D} = \mu \tag{25}$$

or, $\mathbf{D} = \mathbf{B}^{-1}(\omega)\,\mu$, μ being a column matrix.

We must remember here that in going through the previous steps the constraint eqn. (20) was employed appropriately. With the D_i's found we construct

$$\phi_0' = (\phi_0 + \delta\phi_0')(1 + \langle \delta\phi_0' | \delta\phi_0' \rangle)^{-\frac{1}{2}}.$$

(3) We now substitute ϕ_0' in $\{\mathrm{Re}\ K(\Phi)\}$ and solve again for the coefficients C_i^+ and C_i^-, and go back to step 2.

We now keep on looping between steps (2) and (3) until we get a self-consistent set of $\delta\phi_0^+$ $\delta\phi_0^-$ and ϕ_0' Usually four to five cycles suffice for these quantities to converge to within an acceptable limit.

The optimal function $\tilde{\Phi}$ (1,2) may now be used to compute the dynamic polarizability. The expectation value of the dipole moment operator is given by

$$\langle D \rangle = \langle \Phi | \Sigma Z_i | \Phi \rangle / \langle \Phi | \Phi \rangle \qquad (27)$$

where for $\tilde{\Phi}$ we use eq. (14), in which we use the optimal functions $\delta\phi_0^+$, $\delta\phi_0^-$ and ϕ_0'. We then get the following expression for the dynamic polarizability

$$\alpha_d(\omega) = 2\langle \phi_0 | \phi_0' \rangle (\langle \phi_0 | Z | \delta\phi_0^+ \rangle + \langle \phi_0 | Z | \delta\phi_0^- \rangle). \qquad (28)$$

All the above calculations are repeated for other frequencies in the first transition region.

5. Discussions of Numerical Results

(a) *The dynamic polarizability*

The values of the polarizability $\alpha_d(\omega)$ at different frequencies in the first transition region are listed in table 1. The value of $\alpha_d(\omega)$ extrapolated to zero-frequency is found to be 1.370 a.u., which is a substantial improvement on the CHF $\alpha_d(0)$ value 1.322 a.u.[1]. The present value is very close to the accurate result of Schwartz[11], 1.383 a.u., obtained from an extension configuration-interaction calculation. This close agreement indicates that the rearrangement effect incorporates in a very simple but effective manner the major correlation effects that contribute to the polarizability.

At certain values of the impressed frequency ω the dynamic polarizability value goes to infinity; these frequencies correspond to the poles of the Response function for the system and consequently they correspond to the transition energies of the system from the ground state to the excited states. In the present calculation we have located only the first pole, which appears

Table 1. Dynamic polarizability of He at some sample frequencies in the first transition region in a.u.

Frequency	Present results	Coupled Hartree Fock results*
0.0001	1.3704	1.3222
0.005	1.3704	1.3222
0.1	1.3869	1.3362
0.2	1.4397	1.3805
0.3	1.5397	1.4513
0.4	1.7138	1.6007
0.5	2.0310	1.8341
0.6	2.7348	
0.7	6.1801	
0.725	13.6165	
0.730	19.7871	
0.735	40.4260	
0.740	−202.6834	

*Because of the correlation imbalance in the present calculation (see text), the comparison is meaningful only in the long wavelength region.

at a value between 0.735 and 0.74 a.u., and corresponds to the $1S^2$: $^1S \rightarrow$ 1s2p : ^1P transition in the He atom. This value is about 5% lower than the experimental value for this transition which is 0.780 a.u.[12]. The corresponding transition energy found from a purely CHF treatment is 0.797 a.u.[13], which agrees far better with the experimental value, despite the neglect of the rearrangement effect in the CHF calculation. This discrepancy may be understood along the following lines. The inclusion of the rearrangement effect is tantamount to calculating the single excited states self consistently. It is well known that the correlation error in the singly excited states is very small with respect to a single SCF configuration[14], especially in small atoms, essentially due to the fact that the orbitals involved describe different regions space. On the other hand, the correlation error in ground state is much greater. Hence the transition energy in present calculation, being the difference

in the energies of two such SCF configurations, suffers from a correlation unbalance, which depresses the transition energy beneath its true value. In the CHF theory the core orbitals in the singly excited configurations are kept frozen in he HF state, which causes a significant correlation error in the excited state. The relatively more accurate location of the poles in the CHF theory is thus due to a cancellation of the correlation errors in the ground and the excited states.

(b) The oscillator strength for the

$1s^2$: $^1S \rightarrow$ 1s2p : ^1P transition in He

The dynamic polarizability $\alpha_d(\omega)$ may be expressed in terms of the oscillator strengths f_{no} of transition from the ground state to the various excited states n as[15]

$$\alpha_d(\omega) = \sum_{n \neq o}^{\infty} \frac{f_{no}}{\omega_{no}^2 - \omega^2}$$

ω_{no} being the corresponding transition frequency. If the impressed frequency ω be chosen to be very close to a transition frequency ω_{no}, then we may approximately

$$\alpha_d(\omega) \simeq \frac{f_{no}}{\omega_{no}^2 - \omega^2}$$

since this term overwhelmingly dominates over the remaining ones. Considering two frequencies ω_1 and ω_2 in the immediate neighbourhood of ω_{no}, and corresponding values of $\alpha_d(\omega_1)$ and $\alpha_d(\omega_2)$, we may find both f_{no} and ω_{no} from this relation, It may be shown that this procedure is numerically stable. By considering the values of $\alpha_d(\omega)$ at $\omega = 0.735$ a.u. and $\omega = 0.74$ a.u. we arrive at the following values for f_{no} and ω_{no}

$$f_{no} = 0{\cdot}248 \quad \text{a.u.}$$

$$\omega_{no} = 0{\cdot}739 \quad \text{a.u.}$$

where the quantum number n denotes the state 1s2p : ^1P Again, f_{no}, is given by the length formula[15]

$$f_{no} = 2\,\omega_{no} \cdot |\langle n | \sum_i r_i | 0 \rangle|^2.$$

Since the computed transition energy ω_{no} suffers from a correlation imbalance as discussed earlier, it is necessary to use the experimental value $\omega_{no}^{expt.}$ to get a better estimate of the oscillator strength. This is easily done by defining

$$f_{no}^{m} = \left(\omega_{no}^{expt.} \middle/ \omega_{no} \right) f_{no}$$

The value of f_{no}^{m} is found to be 0.262 a.u. in excellent agreement with the result of Weiss[16], 0.276 a.u., found from an extensive configuration-interaction calculation. This result shows once again that the rearrangement effect accounts for the major part of the correlation error in the excited state, at least in the case of He.

The most time-consuming aspect of the present scheme of calculations is the repeated looping between the steps (2) and (3) of section 4 which has to be done four to five times at every frequency to attain proper convergence. We may, however, conceive of a slight modification of the present scheme in which there will be considerable saving in computation time against a slight sacrifice in accuracy. One interesting feature that emerges from the present calculation is that the rearrangement effect is very weakly frequency dependent, i.e., the change in the occupied HF orbital is nearly constant over the whole frequency range. To see this, we have listed in Table II the expectation

Table 2. Expectation value of the one particle operator f with respect to the new occupied orbital ϕ_0' at different frequencies in a.u.*

Frequency	$\langle f \rangle$
0.1	−1.9936
0.2	−1.9945
0.3	−1.9958
0.4	−1.9973
0.5	−1.9987
0.6	−1.9996
0.7	−1.9997
0.735	−1.9997
0.74	−1.9998

*The value of $\langle \phi_0 | f | \phi_0 \rangle$ is −1.9437 a.u. The lower value of $\langle \phi_0' | f | \phi_0' \rangle$ compared $\langle \phi_0 | f | \phi_0 \rangle$ is due to the spatial contraction of ϕ_0' compared to ϕ_0.

value $\langle\phi_0' \mid f \mid \phi_0'\rangle$, where f is the single particle operator part of the unperturbed Hamiltonian, at various frequencies. The near independence of $\langle f \rangle$ on ω suggests that we compute the rearranged wavefunction at some suitable frequency, and use it as an input in eqn. (15) for calculating $\alpha_d(\omega)$ at the other frequencies. In that case the iterations become unnecessary, and the time for calculation becomes comparable to that required in a straightforward CHF calculation. Such a modification is particularly important for application in larger atoms for which the time of computation escalates rapidly

The problem of correlation imbalance between the ground and excited states is the most serious one if further application of the present ideas to larger atoms is contemplated. To overcome this difficulty, the most direct method will be to bring in more configurations, mainly to improve the ground state energy. The present calculation is exploratory, and was aimed just at testing the rearrangement idea. For applications to larger atoms, a more general formulation is required, retaining the essential simplicity and directness of the rearrangement idea. This we hope to develop in future.

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